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Polymerization of Olefins by the Binary Mixture of Organometallic Compound and Silica-Alumina-Titania

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Crystalline Polyaldehydes

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Hirosuke IMAI, and Yoshikazu FUJII

Makromol. Chem., **37**, 149 (1960)

We found that aldehydes such as acetaldehyde propionaldehyde and trichloroacetaldehyde were polymerized by organometallic compound or by metal alkoxide to give crystalline resinous polymer of high molecular weight.

Crystalline polyacetaldehyde was much less soluble in organic solvents than the amorphous one. The infra-red spectrum of crystalline polyacetaldehyde was shown to be sharper than that of amorphous one and to have specific absorption bands, although it indicated also the structure of methyl polyoxymethylene.

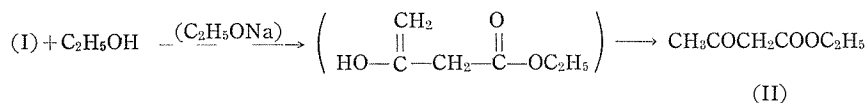
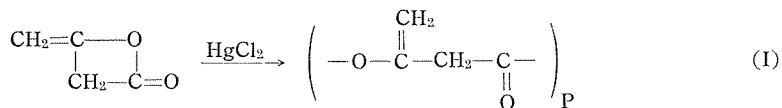
Active species of this polymerization was supposed to be the metal alkoxide.

Polymerization of Diketene

Junji FURUKAWA, Takeo SAEGUSA, Noritoshi MISE,
and Akihiro KAWASAKI

Makromol. Chem., **39**, 243 (1960)

It was found that mercuric chloride polymerized diketene to give the polymer of polyester structure (I). The molecular weight of this polymer was 1630. The structure of the polymer was assumed by the infra-red spectrum. The alkali-alcoholysis of the polymer with ethanol gave ethylacetoacetate (II), and this finding supports the structure (I).

**Polymerization of Olefins by the Binary Mixture of Organometallic Compound and Silica-Alumina-Titania**

Junji FURUKAWA, Takeo SAEGUSA, Teiji TSURUTA, Shiro ANZAI,
Tsuneaki NARUMIYA and Akihiro KAWASAKI

Makromol. Chem., **41**, 17 (1960)

Silica-alumina-titania was prepared by the hydrolysis of a mixture of ethyl orthosilicate, aluminum isopropoxide and ethyl orthotitanate followed by calcination. The catalyst consisting of silica-alumina-titania (wt. ratio 45:5:50) and

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triethylaluminum gave a linear polyethylene (mol. wt. $51.0 \cdot 10^4$) and polypropylene (mol. wt. $22.9 \cdot 10^4$) and the overall energy of activation of the polymerization of ethylene by this catalyst was found to be 6.4 Kcal/mole. The effects of the composition and the temperature of calcination of the silica-alumina-titania were investigated, and some kinetic features of the catalyst were discussed.

In the polymerization of ethylene, this catalytic system is more active than the so-called Phillips catalyst (chromium oxide/silica-alumina) and the so-called Standard catalyst (molybdena-alumina), but less active than the Ziegler catalyst (i.e. $\text{TiCl}_4\text{-AlEt}_3$). The polyethylene produced by this catalyst has little branching and its molecular weight is comparable to that obtained by the Ziegler catalyst.

Polymerization of Propylene Oxide and Vinyl Compounds by Diethylzinc in the Presence of Cocatalysts

Ryozo SAKATA, Teiji TSURUTA, Takeo SAEGUSA
and Junji FURUKAWA

Makromol. Chem., **40**, 64 (1960)

Elastic solid polypropylene oxide was obtained by the following binary systems as catalyst: diethylzinc-oxygen, diethylzinc-water, diethylzinc-methanol and diethylzinc-ethanol. Polymers obtained by the systems containing water, methanol and ethanol involved crystallizable fraction. Alkoxides of zinc play an important role in the polymerization with the systems containing oxygen, methanol and ethanol. The active component of the diethylzinc-water system was a yellow solid substance containing the structures, $\text{C}_2\text{H}_5\text{-Zn-O-Zn-}$ and $\text{C}_2\text{H}_5\text{O-Zn-O-Zn-}$. The diethylzinc-water catalyst obtained by dissolving the yellow solid substance in *n*-hexane was transparent in appearance, but was found to be heterogeneous in character. Vinyl compounds were also polymerized by these catalysts. Polymerization of vinyl compounds is considered to proceed according to a radical mechanism and that of propylene oxide to an ionic mechanism.

Infrared Spectrum and Structure of Polydiketene

Akihiro KAWASAKI, Junji FURUKAWA, Takeo SAEGUSA,
Noritoshi MISE and Teiji TSURUTA

Makromol. Chem., **42**, 25 (1960)

Mercuric chloride polymerized diketene at low temperature. The molecular weight of the acetone-insoluble and dioxane-soluble fraction of the polymer was 1630.

From the alcoholysis of the polymer and the infrared spectrum of the polymer, the molecular structure of the polymer was considered to be the open chain polymer of vinylaceto- β -lactone. Consequently, the molecular structure of diketene